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Y H. Guo

Fudan university Shanghai China

Xuebin Yu

University of Wollongong, xyu@uow.edu.au

L Gao

Fudan University Shanghai China

Guanglin Xia

Fudan University Shanghai China

Zaiping Guo

University of Wollongong, zguo@uow.edu.au

See next page for additional authors

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Authors

Y H. Guo, Xuebin Yu, L Gao, Guanglin Xia, Zaiping Guo, and Hua-Kun Liu

Significantly improved dehydrogenation of LiBH₄ destabilized by TiF₃

Y. H. Guo,^a X. B. Yu,^{*ab} L. Gao,^a G. L. Xia,^a Z. P. Guo^b and H. K. Liu^b

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The hydrogen storage properties of LiBH₄ ball milled with TiF₃ were investigated. It was found that the LiBH₄-TiF₃ mixture exhibited significantly improved dehydrogenation properties. For example, the LiBH₄-TiF₃ (mole ratio: 3 : 1) sample started to release hydrogen at around 100 °C, and the hydrogen desorption capacity reached 5.0 wt% at 250 °C. Furthermore, the dehydrogenated product can be partially rehydrogenated at 100 atm H₂ and 350 °C. X-Ray diffraction (XRD), infrared (IR) spectroscopy and X-ray photoelectron spectroscopy (XPS) characterizations revealed that the decreased dehydrogenation conditions in the LiBH₄-TiF₃ system resulted from an exothermic reaction of 3LiBH₄ + TiF₃ → 3LiF + TiB₂ + B + 6H₂, which improved both its thermodynamics and kinetics. As the above reaction is exothermic, the reverse reaction is not feasible, further investigations indicated that the rehydrogenation may be due to the formation of another borohydride.

Introduction

The hydrogen storage program was proposed and began investigation several decades ago.^{1,2} With the ever-increasing demand for clean and renewable energy sources as a long-term solution for a secure energy future, tremendous efforts have been devoted to the research and development of hydrogen storage materials in the past few decades.³⁻⁷ Up to now, several classes of candidate hydrogen storage materials, including metal hydrides,^{3,4} polymers⁸ and chemical hydrides⁹⁻¹² and organometallic complexes,¹³ *etc.*, have been developed and investigated. Among them, LiBH₄ is a promising hydrogen storage material due to its high hydrogen storage capacities (18.3 wt%, 121 kg m⁻³) which are well above the US Department of Energy's (DOE) target for transportation applications by 2015 (9.0 wt% and 91 kg m⁻³).^{14,15} However, its main evolution of gas starts at 380 °C, and the rehydrogenation can be achieved only under conditions of 15–30 MPa H₂ pressure and 650 °C.¹⁶

To meet all the demands required for commercial vehicular applications, the dehydrogenation/rehydrogenation of LiBH₄ needs to be improved. In 2003, Züttel *et al.* reported that SiO₂

may be used as a catalyst for the dehydrogenation of LiBH₄, lowering the temperature of hydrogen evolution to 300 °C.¹⁷ Then, destabilization and nanocrystallization of LiBH₄¹⁸ were extensively used for the purpose of improving its thermodynamic and kinetic properties. The destabilization involves modifying the thermodynamics of hydrogenation/dehydrogenation reactions by using additives to form compounds or alloys in the dehydrogenated state.¹⁹ Literature protocols showed that many additives, including metals,²⁰ hydrides,²⁰⁻²² chlorides,²² oxides²³ and other materials, such as carbon²⁴ or their mixtures,^{14,25-27} can improve the dehydrogenation and rehydrogenation properties of LiBH₄. Up to now, the most effective composite material reported is LiBH₄ + 0.2MgCl₂ + 0.1TiCl₃, which releases 5 wt% of hydrogen from 60 °C to 400 °C and can be rehydrogenated to 4.5 wt% at 600 °C.²⁷ Meanwhile, first principle calculations were employed and a reasonable thermodynamic guideline, which is beneficial for both assessing the validity and prediction of the destabilization reactions, was proposed.^{19,28}

It has been reported that titanate salts can promote the dehydrogenation and rehydrogenation properties of LiBH₄ and its related multicomounds.^{22,26,27,29} However, the LiBH₄-TiF₃ system was not systemically investigated and the role of TiF₃ is not quite clear. In this paper, the binary composite was studied, superior dehydrogenation performance was observed and the role of TiF₃ in destabilizing LiBH₄ is discussed. The initial desorption properties for the system were evaluated using Sievert's methods

^aDepartment of Material Science, Fudan University, Shanghai, 200433, China. E-mail: yuxuebin@fudan.edu.cn

^bInstitute for Superconducting and Electronic Materials, University of Wollongong, NSW, 2522, Australia

Broader context

It is already known that titanate salts can promote the dehydrogenation and rehydrogenation properties of LiBH₄. In this paper, a promising hydrogen storage binary composite of LiBH₄-TiF₃ was reported. It was found that LiBH₄ can react with TiF₃ to release hydrogen at about 100 °C based on an exothermic reaction of 3LiBH₄ + TiF₃ → 3LiF + TiB₂ + B + 6H₂, which improved both its thermodynamics and kinetics.

Although the reverse reaction in the LiBH₄-TiF₃ system is not thermodynamically favoured, as indicated by the exothermic nature of the dehydrogenation reactions, the dehydrogenated products can be partially rehydrogenated at 350 °C and 100 atm H₂ pressure due to the formation of a new borohydride.

and a thermogravimetric/differential thermal analysis mass spectrometer (TG/DTA-MS). Powder X-ray diffraction (XRD), infrared (IR) spectroscopy and X-ray photoelectron spectroscopy (XPS) were used to determine the sample phase and the dehydrogenation and rehydrogenation pathway. Results show that the onset of hydrogen desorption is only about 100 °C and the LiBH₄-TiF₃ mixture (3 : 1) can release 5.0 wt% and 6.4 wt% hydrogen below 250 °C and 500 °C, *i.e.* both the thermodynamic and the kinetic properties of LiBH₄ can be improved when destabilized by TiF₃. The dehydrogenated sample can also be partially rehydrogenated at 100 atm H₂ and 350 °C. Furthermore, the enthalpy change of the dehydrogenation reaction was calculated, the role of TiF₃ in decreasing the dehydrogenation of LiBH₄ and the rehydrogenation ability were discussed.

Experimental

The source materials were obtained commercially, namely LiBH₄ 95% (Alfa Aesar, USA) and TiF₃ (Alfa Aesar, USA) were used without further purification, with all handling procedures conducted under an argon atmosphere. Approximately 0.5 g mixtures of LiBH₄-TiF₃ with various mole ratios of 50 : 3 (S1), 5 : 1 (S2), 3 : 1 (S3) and 2 : 1 (S4) were mechanically milled for 15 min (planetary QM-1SP2) under argon.

Hydrogen release property measurements were performed by Sievert's method from ambient temperature to 600 °C at a 2 °C min⁻¹ heating rate and by thermogravimetric/differential thermal analysis (TG/DTA, STA 449C) connected to a mass spectrometer (MS, QMS 403) using a heating rate of 10 °C min⁻¹ under a 1 atm argon atmosphere. Typical sample quantities were 5–10 mg, which is sufficient for getting accurate results due to the high sensitivity of the employed equipment. The rehydrogenation of the LiBH₄-TiF₃ sample was carried out on a home-made Sievert's apparatus under 10 MPa hydrogen pressure and 350 °C for 12 h. The pressure-concentration-temperature (PCT) measurements were carried out on a Sievert's apparatus, a named gas reaction controller (GRC, Advanced Materials Corp., USA). For the PCT desorption measurement, the sample was first evacuated at room temperature, and then a starting hydrogen pressure (purity 99.9999%) of 30 atm was applied to the container to about 30 atm. After that, the sample was heated to the desired temperatures. During the desorption, the pressure of the system was measured with a pressure gauge. The equilibrium time for each point was 120 s. The equilibrium time is the default period of time in our program to judge the equilibrium; unless the monitored pressure changes within that period of time (120 s), the program will not go to the next pressure point. Finally, the weight of this volume is calculated and the pressure is plotted as a function of the desorbed amount of hydrogen (in weight percent). The powder X-ray diffraction (XRD, Rigaku D/max 2400) measurements were conducted to confirm the phase structure. Powders were spread and measured on a Si single crystal. Amorphous polymer tape was used to cover the surface of the powder to avoid oxidation during the XRD measurement. Fourier transform infrared spectroscopy (FT-IR, Magna-IR 550 II, Nicolet) analyses were conducted to confirm the reversible formation of B-H bond. The products were pressed with KBr and then loaded in a sealed chamber for the measurement. The oxidation state of the titanium and boron components were

analyzed using X-ray photoelectron spectroscopy (XPS, PHI-5000C ESCA) on a RBD upgraded system (PerkinElmer) with Mg K α radiation ($h\nu = 1253.6$ eV). The binding energy values correspond to the carbon C 1s core level at 284.6 eV.

Results & discussions

The LiBH₄-TiF₃ samples were prepared through ball milling. The temperature programmed desorption (TPD) profile in Fig. 1 shows the hydrogen desorption properties of the ball-milled LiBH₄ and LiBH₄-TiF₃ mixtures. For commercial LiBH₄, no hydrogen is released until 300 °C, but for LiBH₄-TiF₃ (mole ratio: 3 : 1), the majority of the hydrogen is released below 290 °C. It is clear that the decomposition properties of LiBH₄ can be significantly improved by TiF₃ addition. Meanwhile, it can be observed from the dehydrogenation properties of LiBH₄-TiF₃ with different mole ratios (Fig. 2) that when there is sufficient TiF₃ (mole ratio of LiBH₄ : TiF₃ \geq 3 : 1), the dehydrogenation starts from 100 °C and ends at about 290 °C, while insufficient TiF₃ will lead to partial decomposition at temperatures >290 °C.

After heating to 600 °C, a total release of 11.9 wt% hydrogen was observed for commercial LiBH₄, which is 65.0% of its theoretical hydrogen capacity. However, for LiBH₄-TiF₃

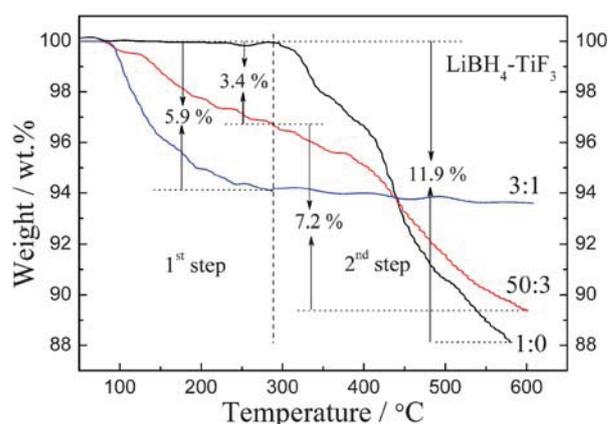


Fig. 1 TPD of the commercial LiBH₄ and LiBH₄-TiF₃ mixtures, with mole ratios of 50 : 3 and 3 : 1. The heating rate is 2 °C min⁻¹.

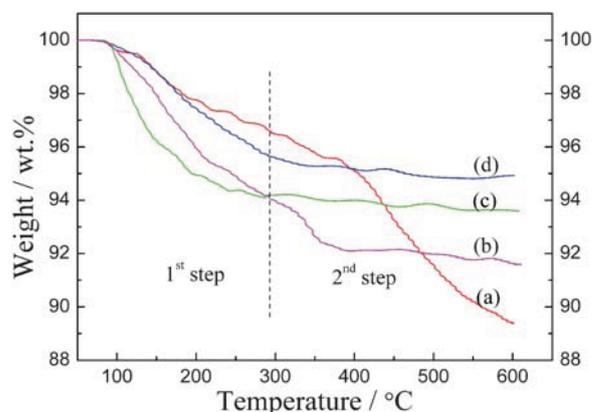


Fig. 2 TPD of the LiBH₄-TiF₃ mixtures with mole ratios of 50 : 3 (a), 5 : 1 (b), 3 : 1 (c), 2 : 1 (d). The heating rate is 2 °C min⁻¹.

(mole ratio: 3 : 1), the weight loss reached 5.9 wt% at 290 °C, corresponding to 83.2% of the hydrogen in LiBH₄. Therefore, TiF₃ addition can promote the decomposition of LiBH₄.

Fig. 3 shows the thermogravimetric/differential thermal analysis (TG/DTA) curves for LiBH₄-TiF₃ (mole ratio: 3 : 1). One step with a total weight loss of 6.0 wt% was observed in the TG curve, which agrees well with the TPD result in Fig. 1. It is also confirmed by the synchronous mass spectroscopy (MS) profile that the gas released is pure H₂. The DTA curve has an endothermic peak at 123.9 °C corresponds to the phase transformation of LiBH₄. The exothermic peak at 269.1 °C is ascribed to a chemical reaction of LiBH₄ with TiF₃, resulting in the dehydrogenation of LiBH₄. This reaction starts at a low temperature with low kinetics but becomes violent at 269.1 °C. However, a two-step weight loss with a total capacity of 11.65 wt% was observed in the TG/DTA curves for LiBH₄-TiF₃ (mole ratio: 50 : 3) (Fig. 4), which agrees well with the TPD result in Fig. 1. Furthermore, the DTA curve showed three endothermic peaks. The endothermic peaks at 122.3 °C, 284.8 °C, and 400–500 °C may correspond to the phase transformation, fusion, and decomposition of LiBH₄, respectively.²⁶ It is clear that insufficient TiF₃ will lead to excess LiBH₄, which decomposes above 290 °C.

Pressure–composition–temperature (PCT) desorption curves for LiBH₄ at 400 °C and LiBH₄-TiF₃ (mole ratio: 3 : 1) at 150 °C, 200 °C, and 250 °C are shown in Fig. 5. Firstly, no flat plateau can be observed in the curves, which is different from the behavior of the traditional metal hydrides. This is specific to this kind of composite as its equilibrium pressure is probably above 30 bar the maximum pressure of our equipment. Secondly, the fact that the desorption capacity of the compound increases with

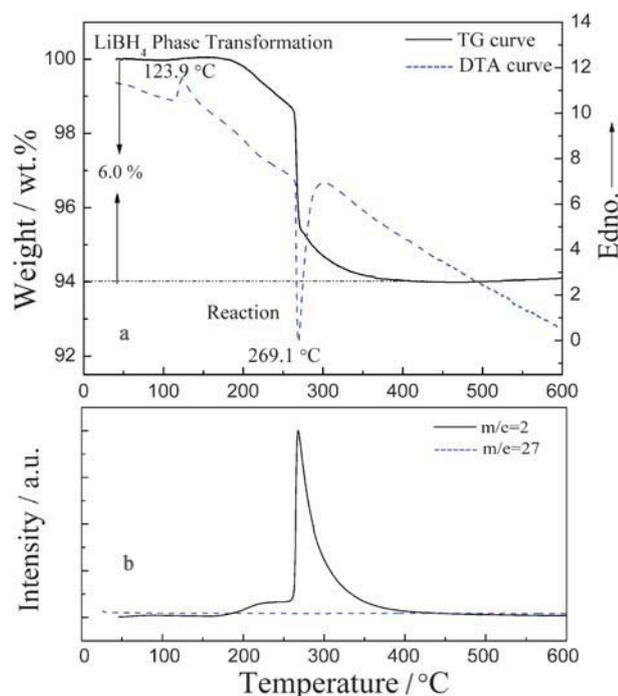


Fig. 3 (a) TG/DTA curves for a LiBH₄-TiF₃ mixture (mole ratio: 3 : 1), and (b) synchronous MS profiles of $m/e = 2$ (H₂), $m/e = 27$ (B₂H₆). The heating rate is 10 °C min⁻¹.

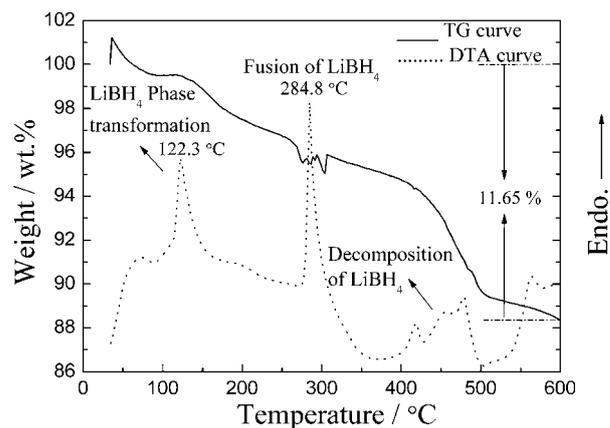


Fig. 4 TG/DTA curves for a LiBH₄-TiF₃ mixture (mole ratio: 50 : 3). The heating rate is 10 °C min⁻¹.

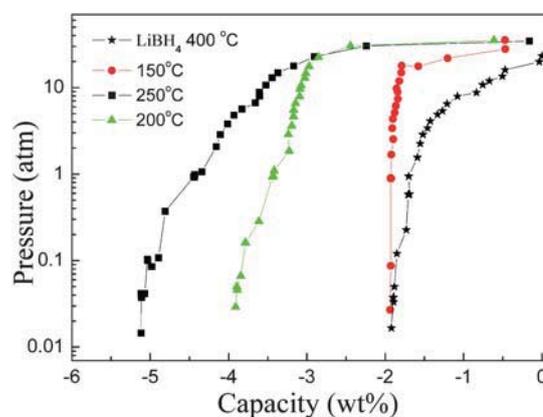


Fig. 5 PCT desorption curves of the commercial LiBH₄ at 400 °C and LiBH₄-TiF₃ mixture (mole ratio: 3 : 1) at various temperatures.

increasing temperature indicates its relatively poor kinetics. Finally, the mixture can release 4.4 wt%, 3.4 wt%, and 2.0 wt% hydrogen to 1 atm at 150 °C, 200 °C, and 250 °C, respectively, while only 1.7 wt% hydrogen is released for pure LiBH₄ at 400 °C. It is clear that the kinetic property for the hydrogen desorption from LiBH₄ was improved.

The product of the LiBH₄-TiF₃ mixture (mole ratio: 3 : 1) dehydrogenated at 350 °C for 2 h was rehydrogenated at 350 °C and 10 MPa H₂. Its TPD result (Fig. 6) shows that the dehydrogenated product can be partially rehydrogenated, and exhibits improved rehydrogenation conditions than that of pure LiBH₄.³⁰ However, the hydrogen capacity at 500 °C was decreased to 4.0 wt%, and the onset hydrogen desorption temperature is about 300 °C, much higher than that of the original mixture. Meanwhile, additional charge–recharge was tested for the first rehydrogenated sample. After dehydrogenation at 450 °C for 2 h, the first reformed mixture was rehydrogenated at 350 °C and 10 MPa H₂ for 12 h. However, only less than 1 wt% hydrogen desorption was achieved, suggesting that the reversibility for the rehydrogenated product is poor. Hence, it is predicted that the rehydrogenation pathway was not the reverse reaction of dehydrogenation.

To understand the dehydrogenating/rehydrogenating process for the LiBH₄-TiF₃ mixtures, X-ray diffraction (XRD) and

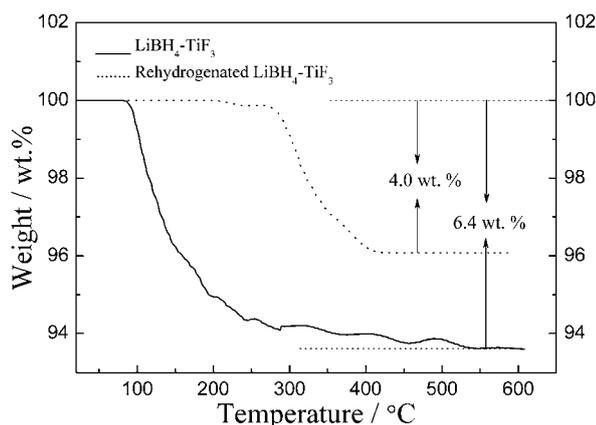


Fig. 6 TPD of $\text{LiBH}_4\text{-TiF}_3$ mixtures (mole ratio: 3 : 1) and its rehydrogenated sample. The heating rate is 2°C min^{-1} .

infrared (IR) spectroscopy measurements were conducted. The XRD patterns for the milled samples before and after dehydrogenation at 600°C are shown in Fig. 7. For the as-prepared $\text{LiBH}_4\text{-TiF}_3$ mixtures, only LiBH_4 and TiF_3 were found in the XRD patterns, implying that the ball milling creates a physical mixture. For the dehydrogenated samples, the LiBH_4 and TiF_3 peaks disappeared. New phases of LiH and LiF were observed for the $\text{LiBH}_4\text{-TiF}_3$ (mole ratio: 50 : 3) mixture, while only the LiF phase is present for the $\text{LiBH}_4\text{-TiF}_3$ (mole ratio: 3 : 1) mixture. Similar results can be observed for $\text{LiBH}_4\text{-TiF}_3$ mixtures with different mole ratios (Fig. 8). In the case of the rehydrogenated sample, no desirable LiBH_4 was observed, but only LiF (Fig. 8). The IR results (Fig. 9) for LiBH_4 and the milled $\text{LiBH}_4\text{-TiF}_3$ (mole ratio: 3 : 1) together with its dehydrogenated and rehydrogenated samples show that the peaks for B–H in the milled $\text{LiBH}_4\text{-TiF}_3$ mixture are similar to the commercial LiBH_4 , which reconfirmed the physical mixture of the ball milling. Meanwhile, the disappeared B–H bond after the dehydrogenation at 350°C reappeared in the regenerated sample, indicating the partial reformation of the B–H bond during the rehydrogenation process.

To identify the states of the elements Ti and B, X-ray photoelectron spectroscopy (XPS) was carried out for the

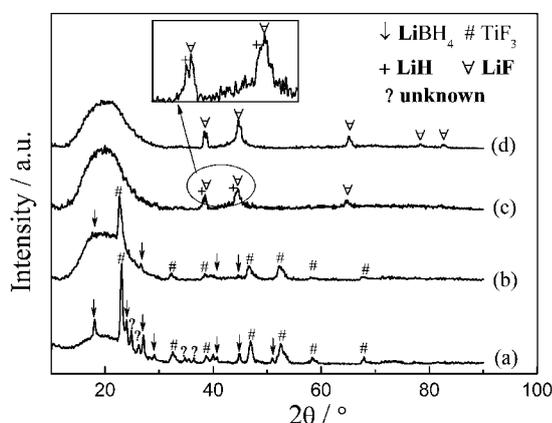


Fig. 7 XRD patterns for the milled $\text{LiBH}_4\text{-TiF}_3$ mixtures (a, b) before and (c, d) after dehydrogenation at 600°C . The mole ratios are 50 : 3 for (a, c) and 3 : 1 for (b, d).

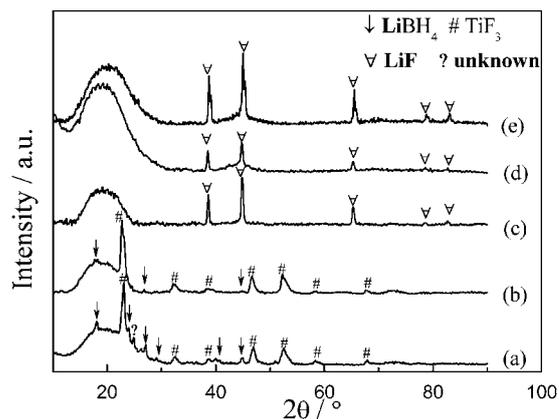


Fig. 8 XRD patterns for the milled $\text{LiBH}_4\text{-TiF}_3$ mixtures (a, b) before and (c, d) after dehydrogenation at 600°C , and (e) the rehydrogenated sample. The mole ratios are 5 : 1 for (a, c), 2 : 1 for (b, d) and 3 : 1 for (e).

dehydrogenated and regenerated $\text{LiBH}_4\text{-TiF}_3$ (mole ratio: 3 : 1) sample. For the sample dehydrogenated at 350°C , as shown in Fig. 10(a), the $\text{Ti}_{2p_{2/3}}$ binding energies at 454.2 eV and 458.9 eV are quite similar to the binding energies of TiB_2 and TiO_2 , respectively. Peaks centered on 187.4 and 192.0 eV are observed for boron, for which the peak at 187.4 eV may be assigned to TiB_2 and the peak at 192.0 eV is assigned to B_2O_3 .^{31–34} The appearance of TiO_2 and B_2O_3 may be due to oxidation in air when the sample was taken out and loaded during the XPS measurement. Similar results (XPS shape and position) can be obtained for the sample dehydrogenated at 600°C , as shown in Fig. 10(b), in which the $\text{Ti}_{2p_{2/3}}$ binding energies are 453.4 eV and 459.4 eV, and the B_{1s} binding energies are 187.0 eV and 192.5 eV. It is clear that the $\text{LiBH}_4\text{-TiF}_3$ mixture produced TiB_2 during the dehydrogenation. For the rehydrogenated sample, as shown in Fig. 10(c), a weak peak and a strong peak centered at 191.8 and 187.4 eV are observed for boron. The peak at 191.8 eV is assigned to B_2O_3 , the peak at 187.4 eV, which is very similar to the 187.2 eV of LiBH_4 (result not shown), may be assigned to regenerated borohydride. The $\text{Ti}_{2p_{2/3}}$ binding energies are 453.5 eV and 458.7 eV, respectively. The peak at 458.7 eV is assigned to TiO_2 , the peak at 453.5 eV is similar to TiB_2 , but as

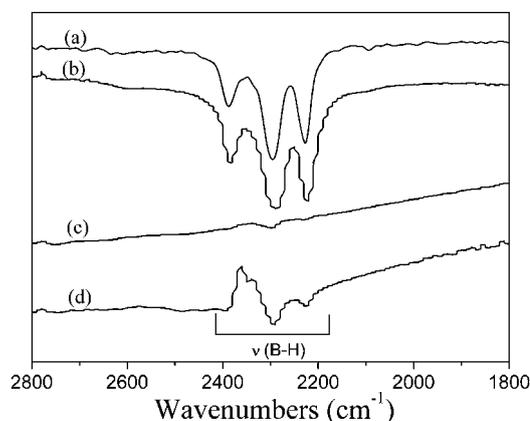


Fig. 9 IR spectrum for commercial LiBH_4 (a), a milled $\text{LiBH}_4\text{-TiF}_3$ mixture (mole ratio: 3 : 1) (b) and the mixture dehydrogenated at 350°C (c) and its rehydrogenated sample (d).

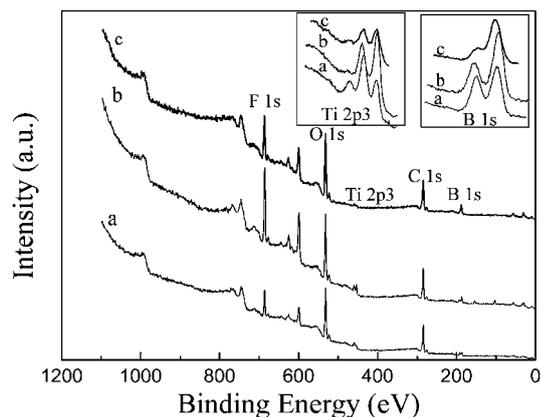
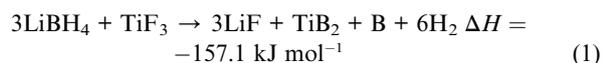


Fig. 10 XPS spectra for a LiBH₄-TiF₃ mixture (mole ratio: 3 : 1) dehydrogenated at 350 °C (a), 600 °C (b) and its rehydrogenated sample (c). The insets show enlargements of the Ti 2p₃ and the B 1s peaks.

the reformation of the B-H bond is confirmed by IR and XPS results, this peak may be assigned to a material composed of elements Ti, B and H. The fact that TiB₂ cannot be identified from the XRD result in Fig. 7 is probably due to its presence in a highly dispersed, nanocrystalline and/or amorphous form.

Based on the above analysis, the reaction path for the LiBH₄-TiF₃ mixtures is postulated to be:



The 100–290 °C decomposition step is mainly based on the equation above, which has a calculated hydrogen capacity of 7.08 wt%. The weight loss of the decomposition step above 290 °C mainly results from the decomposition of the excess LiBH₄, which produces LiH, which has been confirmed by the XRD result in Fig. 7(c). This reaction might be 2LiBH₄ → 2LiH + 2B + 3H₂.

The standard formation enthalpies for LiBH₄, TiF₃, LiF, and TiB₂ are -190,³⁵ -1435.53, -616.931, and -323.8 kJ mol⁻¹,³⁶ respectively. Therefore, the enthalpy change for the formation of H₂ in reaction (1) is -26.2 kJ mol⁻¹, and this may explain the appearance of the exothermic peak in the DTA curve very well. The standard enthalpy for the decomposition of LiBH₄, namely, ~67 kJ mol⁻¹ for the formation of H₂,³⁷ is endothermic. However, the new pathway is quite different, namely, exothermic, and this may be the reason why the mixture can release hydrogen at a lower temperature. However, the exothermic reaction appears to be thermodynamically unfavorable for rehydrogenation. As the regeneration of the B-H bond was confirmed by the IR spectrum, it is predicted that the rehydrogenation may be due to the formation of another borohydride.

Conclusions

In summary, we have demonstrated that LiBH₄-TiF₃ mixtures exhibit superior dehydrogenation performance. As TiF₃ can react with LiBH₄, the thermodynamics and kinetics of hydrogen release from LiBH₄ are significantly improved, decreasing the

onset of hydrogen desorption to about 100 °C and the LiBH₄-TiF₃ mixture (3 : 1) can release 5.0 wt% and 6.4 wt% hydrogen below 250 °C and 500 °C. Meanwhile, the dehydrogenated sample is partially reversible at 100 atm H₂ and 350 °C, with the hydrogen capacity for the rehydrogenated sample decreased to 4.0 wt% at 500 °C. Additionally, the reversibility was probably not due to the reverse hydrogen desorption reaction, but the formation of another new borohydride which showed worse reversibility.

Acknowledgements

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